

## 7. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting, measuring, and/or monitoring iodine, its radioisotopes, its metabolites, and other biomarkers of exposure and effect to iodine. The intent is not to provide an exhaustive list of analytical methods. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to for environmental samples are the methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by a trade association such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that modify previously used methods to lower detection limits, and/or improve accuracy and precision.

### 7.1 BIOLOGICAL MATERIALS

Entry of iodine and its radioisotopes into the human body can be gained through ingestion, inhalation, or penetration through skin (IAEA 1988; NCRP 1985). The quantities of iodine within the body can be assessed through the use of bioassays that are comprised of either *in vivo* measurements and/or *in vitro* measurements. *In vivo* measurements can be obtained through techniques that directly quantitate internally-deposited iodine using, for example, thyroid or whole body counters. These *in vivo* measurement techniques are commonly used to measure body burdens of iodine radioisotopes, but cannot be used to assess the stable isotope of iodine. Instead, *in vitro* measurements provide an estimate of internally deposited iodine (both the stable and radioactive isotopes), utilizing techniques that measure iodine in body fluids, feces, or other human samples (Gautier 1983). Examples of these analytical techniques are given in NCRP Report No. 87 (1987) and are also listed in Table 7-1.

#### 7.1.1 Internal Iodine Measurements

*In vivo* measurement techniques are the most direct and widely used approach for assessing the burden of iodine radioisotopes within the body. The *in vivo* measurement of these radioisotopes within the body is performed with various radiation detectors and associated electronic devices that are collectively known as *in vivo* thyroid monitors or whole body counters, depending on the body site of interest. These radiation detectors commonly utilize sodium iodide (NaI), hyperpure germanium, and organic liquid scintillation detectors to measure the gamma rays and x-rays emitted from  $^{125}\text{I}$  and  $^{131}\text{I}$ .

**Table 7-1. Analytical Methods for Determining Iodine in Biological Samples**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine	Sample purified on Dowex 1x8 resin column; dried resin fused with NaOH/KNO <sub>3</sub> , dissolved in water; dry 0.5 mL aliquot on polythene sheet; irradiated, dissolved in water with iodine carrier; extracted with trioctylamine/xylene; back extracted with 1 N ammonia, precipitate as AgI <sub>2</sub>	INAA (γ-ray spectrometry)	0.01 µg/L	94%	Ohno 1971
Urine	Sample digested in chloric acid; arsenious acid added and then submitted for automated analysis	As-Ce catalytic spectrophotometry	between 0.01–0.06 µg per sample (0.02–0.50 mL sample volume)	96–97%	Benotti and Benotti 1963; Benotti et al. 1965
Thyroid	Powdered or fresh tissue digested with H <sub>2</sub> SO <sub>4</sub> ; iodide converted to Al <sub>2</sub> I <sub>6</sub> , neutron irradiated; iodine precipitated with Pd	Neutron activation plus mass spectrometry	0.11–2.17 mg/g (range of measured values)	No data	Ballad et al. 1976, Boulos et al. 1973, Oliver et al. 1982
Adipose tissue	Sample placed into polyethylene vials and neutron irradiated	INAA (γ-ray spectrometry)	1.4–8.6 µg/g	No data	EPA 1986

**Table 7-1. Analytical Methods for Determining Iodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Non-thyroid tissues	Tissue samples lyophilized, sealed in polyethylene film, and irradiated with epithermal neutrons using a boron nitride shield	INAA ( $\gamma$ -ray spectrometry)	9.4–2,880 ng/g (range of measured values)	No data	Hou et al. 1997b
Tissues	Aqueous NaOH and Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> added to tissue homogenates; ashed; residue dissolved in water and then injected into an HPLC for the separation of components on a two-column system followed by quantitation of iodine by UV	HPLC with UV detection	0.07–1,060 $\mu$ g/g (range of measured values)	87–97%	Andersson and Forsman 1997
Plasma (protein bound)	Protein precipitated by Somogyi's zinc sulfate reagent, digested in CrO <sub>3</sub> , purified by distillation	As-Ce catalytic spectrophotometry	0.01 $\mu$ g/mL	75–100% (0.01–0.05 $\mu$ g/mL)	Barker 1948
Feces	Dried; pulverized; digested in HNO <sub>3</sub> /HF; treated with HCl/HNO <sub>3</sub>	ICP-AES	0.1 $\mu$ g/mL	88–90%	Que Hee and Boyle 1988
Feces	Dried; pulverized; digested in chloric acid; arsenious acid added and then submitted for automated analysis	As-Ce catalytic spectrophotometry	between 0.01–0.06 $\mu$ g per sample (20–30 mg sample size)	97–101%	Benotti and Benotti 1963, Benotti et al. 1965

**Table 7-1. Analytical Methods for Determining Iodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Milk, serum	Sample is mixed with acetonitrile (1:2), centrifuged; supernatant dried; dissolved in acetonitrile/water and a 1 mL aliquot derivatized with 2-iodosobenzoate in phosphate buffer containing 2,6-dimethyl-phenol	HPLC with UV detection	0.5 µg/L	97.6–102.4%	Verma et al. 1992
Milk, yogurt, cream	Sample incubated in two parts (v:v) methanol; filtered; 4 mL filtrate passed through Sep-Pak C <sub>18</sub> cartridge; final 2 mL of eluate filtered; 100 µL aliquot analyzed by HPLC	HPLC with amperometric detection	25 µg/L	92–114%	Chadha and Lawrence 1990
Bread	Bread is dried; ground; treated with 2N Na <sub>2</sub> CO <sub>3</sub> plus 1% KClO <sub>3</sub> ; dried; incinerated; dissolved; analyzed by the ceric arsenite reaction	As-Ce catalytic spectrophotometry	0.05 µg/g	No data	Sachs et al. 1972

As-Ce catalytic spectrophotometry = arsenious-ceric ion catalytic spectrophotometry; HPLC = high performance liquid chromatography; ICP-AES = inductively coupled plasma-atomic emission spectrometry; INAA = instrument neutron activated analysis; UV = ultraviolet/visible

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The gamma-ray and x-ray photopeaks that are commonly used in the detection and quantitation of these iodine radioisotopes are the 28 keV (0.0665 photons/transition) gamma-ray and/or the  $K_{\alpha 1}$  (27.5 keV, 0.739 photons/transition),  $K_{\alpha 2}$  (27.2 keV, 0.397 photons/transition),  $K_{\beta 1}$  (31.0 keV, 0.140 photons/transition), and  $K_{\beta 2}$  (31.7 keV, 0.043 photons/transition) x-rays for  $^{125}\text{I}$ , and the 364 keV gamma-ray for  $^{131}\text{I}$  (Jönsson and Mattsson 1998; Landon et al. 1980; Palmer et al. 1976). The third iodine radioisotope that is commonly encountered in the environment,  $^{129}\text{I}$ , is difficult to quantitate using *in vivo* monitoring and scanning techniques due to its low specific activity (0.17 mCi/g), low abundance in the environment, and low energy  $\beta^-$  (150 keV) and gamma (40 keV) radiation (NCRP 1983).

Because approximately 20–30% of the iodine that enters the body is taken up by the thyroid gland, *in vivo* thyroid monitoring is preferably and reliably used for assessing  $^{125}\text{I}$  and  $^{131}\text{I}$  burdens in exposed individuals (Bartolini et al. 1988; Bhat et al. 1973; Blum and Liuzzi 1967; Jacobson et al. 1978; Jönsson and Mattsson 1998; Landon et al. 1980; Mandó and Poggi 1988; Nishiyama et al. 1980; Palmer et al. 1976; Plato et al. 1976; Pomroy 1979). As such, *in vivo* thyroid scanning techniques are routinely used to assess thyroid burdens of  $^{125}\text{I}$  and  $^{131}\text{I}$  in individuals with occupational exposures to these radioisotopes; for example, medical personnel, laboratory technicians, nuclear medicine staff, radiochemists, and personnel involved with nuclear fuel processing. The relatively low attenuation of the gamma rays emitted from  $^{131}\text{I}$  by most tissues allows for whole body and thyroid scanning techniques to be utilized in quantitating this iodine radioisotope within an individual (Berg et al. 1987; Nishiyama et al. 1980). Attenuation of lower energy gamma-ray and x-ray emissions for  $^{125}\text{I}$  through tissues is greater than what is observed for the higher energy  $^{131}\text{I}$  gamma-ray. However, the position and close proximity of the thyroid at the base and surface of the neck helps to minimize the effect that attenuation can have on the detection and quantitation of  $^{125}\text{I}$  in the thyroid, as compared to deeper tissues.

Many configurations of the thyroid and whole body counter and scanning methods have been utilized for monitoring and quantitating thyroid iodine radioisotope burdens, ranging from unshielded single-crystal field detectors to shielded, multi-detector scanning detectors (IAEA 1962, 1970, 1972, 1976, 1985; NCRP 1987; Palmer et al. 1976; Plato et al. 1976). The minimum detectable activity of these devices is typically around 30–300 pCi for thyroid monitoring and approximately 2 nCi for whole body scanners (Nishiyama et al. 1980; Palmer et al. 1976; Plato et al. 1976). Where appropriate, shielding of the room that houses the thyroid or whole body counter can be used to increase the detection sensitivity of the equipment by minimizing background radiation. To further insure that internalized iodine radioisotopes are accurately measured, removal of external contamination with radioactive iodine or other gamma-emitting radioisotopes on the clothing or skin of the individual to be scanned is recommended (Palmer et al. 1976). Also, *in vitro* measurements of iodine (see Section 7.1.2) can be used in conjunction with *in vivo* thyroid monitoring when assessing individuals working with iodine radioisotopes, especially in the assessment of individuals who have experienced accidental or routine exposures to iodine radioisotopes (Bhat et al. 1973; Nishiyama et al. 1980).

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Calibration of thyroid and whole body counts is achieved through the use of tissue-equivalent phantoms. These phantoms are constructed to mimic the shape and density of the anatomical structure using tissue equivalent materials such as water-filled canisters or masonite (Bhat et al. 1973; Jönsson and Mattsson 1998; Landon et al. 1980; Nishiyama et al. 1980; Palmer et al. 1976; Plato et al. 1976). An example of a neck phantom is a polyethylene or Lucite cylindrical container filled with water to approximate the dimensions and density of the neck (Jönsson and Mattsson 1998; Landon et al. 1980; Palmer et al. 1976; Plato et al. 1976). Radioiodine standards are measured either as point sources along the phantom or, more typically, dissolved within two water-filled polyethylene or glass tubes (1–2.5 cm in diameter by 5–7 cm in length) that are set at an appropriate distance apart to approximate the positioning of the two lobes of the thyroid glands in the base of the neck. The dimensions of the Lucite and polyethylene neck phantoms are varied to more accurately mimic the actual ranges of adult and children's neck sizes (Palmer et al. 1976; Plato et al. 1976; Pomroy 1979). Other types of modified thyroid-neck phantom models and whole body phantoms have been used to calibrate radioiodine measurements as well (Nishiyama et al. 1980). Comparisons of the actual counting rates obtained from the phantom and the known activity of the radioiodine standards are used to determine the efficiency of the counting technique and, thus, provide the basis for calibration.

Assessment of short- and long-term retention of iodine radioisotopes must take into account the turnover rate for radioiodine within the human body. For  $^{125}\text{I}$ , the mean effective half-life within the body is 37–39 days (Bartolini et al. 1988; Landon et al. 1980); for  $^{131}\text{I}$ , the mean effective half-life is 5–7.6 days (Bhat et al. 1973). These values are much less than the actual biological half-life of iodine ( $^{127}\text{I}$ ) in the body of 96–138 days (Bartolini et al. 1988; Landon et al. 1980), due to the relatively short physical half-lives of these radioisotopes. For acute and chronic exposures to radioiodine, the estimates of radioiodine retention are best calculated from results of multiple thyroid or whole-body measurements. This is because of individual variability in thyroid uptake rates, excretion rates, and uncertainties in determining uptake of radioiodine through inhalation, ingestion, and the skin (Landon et al. 1980; Mandó and Poggi 1988). However, direct comparisons between laboratories of body burdens and clearance rates for specific radioisotopes can be complicated by the differing whole body measurement techniques, calibration methods, and methods used to account for normal background radiation counts that are utilized within the different laboratories.

### 7.1.2 External Measurements

*In vitro* analyses of iodine are routinely performed in situations where *in vivo* analyses cannot be obtained or in support of an *in vivo* monitoring program. Urine is the preferred sample for *in vitro* analyses of iodine, although other sample types, such as feces, tissue, blood, serum, and hair, also can be used on a more limited basis with good detection sensitivities that are typically on the order of <1 µg per sample (NAS 1974). Urine provides for an analysis of soluble iodine, fecal analysis can be used to assess the

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fraction of ingested iodine not absorbed by the gut, and tissue is used to assess whole or regional body burdens of iodine (NCRP 1987).

The *in vitro* analysis of the stable isotope of iodine,  $^{127}\text{I}$ , in commonly acquired human samples (e.g., urine, tissue, feces) is performed by a number of methods that have the selectivity and/or sensitivity to measure iodine in biological matrices (Table 7-1). These methods include arsenious-ceric ion catalytic spectrophotometry, instrumental neutron activation analysis (INAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), and high performance liquid chromatography/ultra-violet-visible detection techniques (Andersson and Forsman 1997; Barker 1948; Benotti and Benotti 1963; Benotti et al. 1965; Cornelis et al. 1975; EPA 1986; Hou et al. 1997b; Ohno 1971; Que Hee and Boyle 1988). The INAA and ICP-AES methods offer the greatest sensitivity for the detection of iodine in human samples (Table 7-1). An example of an application of INAA to the measurement of iodine in urine involves a prepurification of the urine sample to remove interfering ions, such as bromide, upon activation by neutrons (photopeaks are 0.45 MeV for  $^{128}\text{I}$  and 0.55 MeV for  $^{82}\text{Br}$ ). The urine sample is first passed over Dowex 1X8 anion exchange resin, and then followed by the fusion of the washed and dried resin with NaOH/HNO<sub>3</sub>. The fusion residue is dissolved in water with a 0.5 mL aliquot transferred to a polyethylene sheet and dried. The sample is then irradiated with neutrons, dissolved in a solution containing a iodide carrier, extracted with trioctylamine/xylene, back extracted first with 1 M sodium nitrate to remove bromine and then back extracted into 1 N ammonia. From here, the iodine is precipitated as silver iodide, filtered, and analyzed by gamma spectrometry (Ohno 1971).

For the *in vitro* analysis of the iodine radioisotopes,  $^{125}\text{I}$  and  $^{131}\text{I}$ , in human samples, there are a number of the analytical methods that can measure these radioisotopes directly in the samples without the requirement for an extensive sample preparation procedure (Table 7-2), as has been demonstrated for other radioisotopes (Gautier 1983). In the radiochemical analysis of radioiodine in urine, a 24-hour urine collection (approximately 2 L) is obtained followed by the transfer of a 1 L aliquot to a Marinelli beaker for counting in a gamma ray spectrometer. This simple procedure offers high recoveries of 98% and the minimum detection sensitivity 100 pCi/L that is required to evaluate individuals for exposures to  $^{125}\text{I}$  and  $^{131}\text{I}$ . Similar methods can also used for the analysis of these iodine radioisotopes in tissues, feces, blood, milk, and food (AOAC 1984; Baratta and Easterly 1989; Ekman et al. 1967; Gautier 1983).

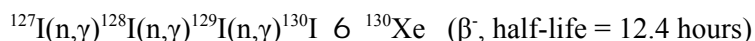
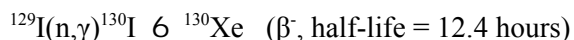
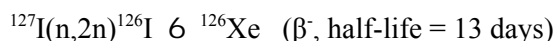
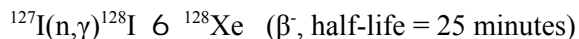
**Table 7-2. Analytical Methods for Determining Radioiodine in Biological Samples**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine	Sample transferred to Marinelli beaker and counted	$\gamma$ -spectrometry with NaI detector	100 pCi/L ( $^{131}\text{I}$ )	98%	Gautier 1983
Thyroid	$^{129}\text{I}$ counted directly in thyroid tissue	X-ray spectrometry with HP Ge detector	0.04 pCi/g ( $^{129}\text{I}$ )	No data	Van Middlesworth 1993
Thyroid	Powdered or fresh tissue digested with $\text{H}_2\text{SO}_4$ ; iodide converted to $\text{Al}_2\text{I}_6$ ; neutron irradiated, and iodine precipitated with Pd	Neutron activation and mass spectrometry	45 pg/g ( $^{129}\text{I}$ )	No data	Boulos et al. 1973, Oliver et al. 1982
Thyroid and other tissues	Tissue sample were lyophilized and ground; pyrolyzed in $\text{O}_2/\text{N}_2$ stream; iodine absorbed onto charcoal; iodine liberated from charcoal by heating; isolated by distillation on cooled glass and then neutron irradiated	INAA with Ge(Li) $\gamma$ -spectrometry	18–74 fCi/g ( $^{129}\text{I}$ )	85% (thyroid) 50–60% (other tissues)	Handl et al. 1990
Saliva	Saliva samples obtained and directly counted	Scintillation counter	1.26–36.5 nCi/mL (range of measured values) ( $^{125}\text{I}$ )	No data	Nishizawa et al. 1985
Feces	Sample directly counted in detector	$\gamma$ -spectrometry with NaI detector	0.14 nCi/L ( $^{131}\text{I}$ )	No data	Lipsztein et al. 1991
Cow's milk	Sample (50–100 mL) directly counted in iron shielded gamma spectrometer	$\gamma$ -spectrometry with NaI detector	4–100 pCi/L (range of measured values) ( $^{131}\text{I}$ )	No data	Ekman et al. 1967
Cow's milk	Conversion of iodine to iodide; concentrated on anion exchange resin; extracted through $\text{CCl}_4$ , water, then toluene	Liquid scintillation counter	0.3 pCi/L ( $^{129}\text{I}$ )	58% raw milk, 80% pasteurized milk; with 30 mg iodine carrier	Gabay et al. 1974
Food	Food samples directly counted in gamma-ray spectrometer	$\gamma$ -spectrometry with NaI or Ge(Li) detector	0.05 pCi/g ( $^{131}\text{I}$ )	No data	Cunningham et al. 1989, 1994

HP = high purity; INAA = instrument neutron activation analysis

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For the quantitation of  $^{129}\text{I}$ , more sensitive methods are required than those described above for  $^{125}\text{I}$  and  $^{131}\text{I}$  (Table 7-2). One approach utilizes the transmutation of the  $^{129}\text{I}$  isotope to another isotope that can be quantitated using mass spectrometric techniques. For example, neutron activation of iodine extracted from thyroid tissues, followed by noble gas mass spectrometry analysis of the resulting xenon isotopes, has been used to measure  $^{129}\text{I}$  and the  $^{129}\text{I}/^{127}\text{I}$  ratio in these tissues (Boulos et al. 1973). This procedure uses the measurement of  $^{126}\text{Xe}$ ,  $^{128}\text{Xe}$ , and  $^{130}\text{Xe}$  isotopes that are formed in the decay of the iodine isotopes,  $^{126}\text{I}$ ,  $^{128}\text{I}$ , and  $^{130}\text{I}$ , to determine the amount  $^{129}\text{I}$  and  $^{127}\text{I}$  in tissue extracts (see below).



Both the ratio of  $^{130}\text{Xe}/^{128}\text{Xe}$  and  $^{130}\text{Xe}/^{126}\text{Xe}$  will be proportional to the ratio of  $^{129}\text{I}/^{127}\text{I}$  in the extract. The method is able to provide a detection sensitivity that is sufficient to measure  $^{129}\text{I}$  as low as 45 pg/g tissue and/or a ratio of  $^{129}\text{I}/^{127}\text{I}$  of  $10^{-10}$ . In those cases where INAA methods cannot be applied due to a large sample set size, availability of an appropriate reactor, the short half-life of the isotope of interest (e.g.,  $^{130}\text{I}$ ), or the cost of activation, there are other techniques available to enhance the detection sensitivity for the  $^{129}\text{I}$  isotope (Gabay et al. 1974). For example, preconcentration of  $^{129}\text{I}$  using anion exchange methods in addition to purifying the sample of interfering materials has been used successfully to analyze samples containing low amounts of  $^{129}\text{I}$  (Gabay et al. 1974, Table 7-2). Also, inductively coupled plasma-mass spectrometry (ICP-MS) methods have been used to quantitate iodine in biological samples using differing sample preparation methods, including Schöniger combustion and extraction methods, providing limits of detection (50 and 0.3 ng/g, respectively) that are appropriate for performing trace analysis of iodine in a large number of environmental and biological samples (Gélinas et al. 1998).

Accuracy of *in vivo* and *in vitro* measurements of iodine and its radioisotopes is determined through the use of standard, certified solutions or radioactive sources with known concentrations or activities of iodine. National Institute of Standards and Technology (NIST) traceable standards for  $^{125}\text{I}$  and  $^{127}\text{I}$  can be obtained through a number of commercial sources. The primary source of certified iodine radioisotope standards is the NIST. Standard reference materials (SRM) for  $^{129}\text{I}$  (SRM 4401LZ, 30MBq [0.8 mCi]) and  $^{131}\text{I}$  (SRM 4949C, 17 kBq [0.45  $\mu\text{Ci}$ ]) are available from NIST. SRMs are also available for  $^{127}\text{I}$  measurements, including SRM 909 (serum), SRM 1486 (bone meal), SRM 1548 (mixed diet), SRM 1549 (nonfat milk powder), SRM 1846 (infant formula), and SRM 2383 (baby food).

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## 7.2 ENVIRONMENTAL SAMPLES

There are two common approaches for measuring iodine radioisotopes in the environment. Iodine radioisotopes can either be measured directly in the field (*in situ*) using portable survey instruments or samples can be procured from the field and returned to the laboratory for quantitation of iodine. However, quantitation of the stable iodine isotope in environmental samples is generally conducted in the laboratory.

### 7.2.1 Field Measurements of Iodine

*In situ* measurement techniques are extremely useful for the rapid characterization of radionuclide contamination in the environment, such as soils, sediments, and vegetation, or when monitoring personnel for exposure to radionuclides. The measurement of gamma-ray-emitting radionuclides in the environment is conducted with portable survey instruments such as Gieger-Mueller detectors, sodium iodide scintillation detectors, and gamma-ray spectrometers. However, the use of gamma-spectrometers in field survey equipment is preferred for measuring  $^{131}\text{I}$  in the field because of its selectivity and sensitivity (EML 1997). The energy and penetrance of the gamma-rays that are emitted during the decay of  $^{131}\text{I}$  provides an advantage for assessing the level of iodine both on and below the surface using portable field survey instruments such as the gamma-ray spectrometer (EML 1997). These gamma-ray spectrometers are equipped with a high purity germanium detector that is able to resolve the 364 keV gamma-ray emitted from  $^{131}\text{I}$  from the gamma-rays emitted from other radionuclides; for example,  $^{40}\text{K}$  (NRC 1997). The concentration and distribution of  $^{131}\text{I}$  that have been detected in the field will need to be determined by laboratory-based analyses of soil samples procured from the survey area.

### 7.2.2 Laboratory Analysis of Environmental Samples

Analytical methods for quantifying iodine and iodine radioisotopes in environmental samples (e.g., air, water, soil, biota, and food) are summarized in Tables 7-3 ( $^{127}\text{I}$ ) and 7-4 ( $^{125}\text{I}$ ,  $^{129}\text{I}$ , and  $^{131}\text{I}$ ). The methods that are commonly used in the analysis of  $^{127}\text{I}$  are based on instrument-based analytical techniques, such as spectrophotometry, electrochemistry, INAA, mass spectrometry (MS), and some colorimetric techniques. The analysis of  $^{125}\text{I}$ ,  $^{129}\text{I}$ , and  $^{131}\text{I}$  can be determined either as total mass or total activity, depending on the analytical technique that is used. Typically, radiochemical methods of analysis employing gamma-ray spectrometry and  $\beta$ - $\gamma$  coincidence scintillation techniques are used to quantitate  $^{125}\text{I}$  and  $^{131}\text{I}$  in environmental samples. However, more sensitive analytical techniques, such as INAA and MS, are typically required to analyze  $^{129}\text{I}$  in environmental samples (Lindstrom et al. 1991; Stephenson and Motycka 1994). Neutron activation and mass spectrometric methods are especially useful, since the amount of  $^{129}\text{I}$  in a sample is often expressed in proportion to amount of  $^{127}\text{I}$  in the same sample

**Table 7-3. Analytical Methods for Determining Iodine in Environmental Samples**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Aerosol (ambient)	Aerosols collected using an Anderson cascade impactor; iodine separated from filters by ignition and adsorbed onto charcoal; extracted from charcoal using NaOH solution; acidified; extracted into CCl <sub>4</sub> as iodine; back extracted into dilute H <sub>2</sub> SO <sub>4</sub> and precipitated as PdI <sub>2</sub> , then neutron irradiated	INAA with Ge $\gamma$ -ray detector	1.68–4.23 ng/m <sup>3</sup> (range of measured values)	No data	Tsukada et al. 1991
Air (ambient)	A known volume of air is passed through a multistage filter assembly; filters extracted in a heated NaOH/Na <sub>2</sub> SO <sub>3</sub> solution containing <sup>129</sup> I <sup>-</sup> as an internal standard; filtered; acidified; iodide precipitated as AgI; filtered; precipitate dissolved in aqueous NH <sub>3</sub> and analyzed	IDMS	0.02–0.024 ng/m <sup>3</sup> (for an average air volume of 70 m <sup>3</sup> )	97–99%	Gäbler and Heumann 1993
Air (occupational)	A known volume of air is drawn into a glass tube containing 150 mg of charcoal; iodine extracted into 0.01 M Na <sub>2</sub> CO <sub>3</sub> using an ultrasonic bath; filtered; injected into ion chromatograph	Ion chromatography	0.45 $\mu$ g/mL	101%	Kim et al. 1981
Water and waste water (EPA Method 345.1)	CaO added to sample; filtered; sodium acetate/acetic acid then bromine water added; excess bromine with sodium formate removed; KI and H <sub>2</sub> SO <sub>4</sub> , titrate added with phenylarsine oxide or sodium thiosulfate using starch indicator	Colorimetric	2–20 mg/L (range of measured values)	80–97% (4.1–21.6 mg/L)	EPA 1983
Water	Sample acidified with HCl; oxidized with H <sub>2</sub> O <sub>2</sub> or KMnO <sub>4</sub> ; treated with NaSO <sub>3</sub> to remove excess oxidant; titrated with KIO <sub>3</sub>	Spectrophotometry	25 $\mu$ g/L–6.35 mg/L	-100% at 0.13–6.35 mg/L	Pesavento and Profumo 1985

**Table 7-3. Analytical Methods for Determining Iodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Water (iodide+iodate)	Ascorbic acid (2%) added to sample; 5 minute stand; reacted with acidified $\text{NaNO}_2$ ; evolved iodine extracted into xylene and analyzed at the emission intensity for iodine of 178.28 nm	ICP-AES	1.6 $\mu\text{g/L}$	95–103%	Miyazaki and Bansho 1987
Water (iodide)	Sample reacted with acidified $\text{NaNO}_2$ ; evolved iodine extracted into xylene; back extracted into 0.5 % aqueous ascorbic acid and analyzed at the emission intensity for iodine of 178.28 nm	ICP-AES	1.6 $\mu\text{g/L}$	97–102%	Miyazaki and Bansho 1987
Water (iodine species)	Samples divided and spiked with $^{129}\text{I}^-$ or $^{129}\text{IO}_3^-$ ; oxidized with UV or $\text{HNO}_3/\text{H}_2\text{O}_2$ (total I), or concentrated/purified on an anion exchange column ( $\text{I}^-$ , $\text{IO}_3^-$ ; anionic organoiodine); samples are then reduced with $\text{Na}_2\text{SO}_3$ and precipitated as $\text{AgI}$	IDMS	0.5 $\mu\text{g/L}$ ( $\text{I}^-$ ) 0.1 $\mu\text{g/L}$ ( $\text{IO}_3^-$ ) 0.2 $\mu\text{g/L}$ (anionic organoiodine) 0.05 $\mu\text{g/L}$ (total iodine)	No data	Reifenhäuser and Heumann 1990
Drinking water	Sample separated on a Dionex AS12 analytical HPLC column; the eluted iodate reacted with acidified bromide in post-column reaction to form tribromide that is detected at 267 nm	HPLC with UV detection	0.05 $\mu\text{g/L}$	110–111% (at 0.5–2.0 $\mu\text{g/L}$ )	Weinberg and Yamada 1997
Tap water	Sample acidified to 0.1 mN nitric acid + $\text{Hg}^{+2}$ (as $\text{Hg}(\text{NO}_3)_2$ ) added to 300 $\mu\text{g/L}$ ; 20 $\mu\text{L}$ aliquot injected into atomizer	Electrothermal atomic absorption spectrometry	3.0 $\mu\text{g/L}$	94.8–104.4% (at 5–20 $\mu\text{g/L}$ )	Bermejo-Barrera et al. 1994
Fresh water (total iodine)	Iodine-iodide is directly measured in water sample	As-Ce catalytic spectrophotometry	0.1 $\mu\text{g/L}$	100%	Jones et al. 1982
Fresh water (iodate)	Iodine-iodide is removed from sample through extraction into chloroform as ion-pair with tetraphenylarsonium cation	As-Ce catalytic spectrophotometry	0.1 $\mu\text{g/L}$	-100% (at 2 $\mu\text{g/L}$ iodate)	Jones et al. 1982

**Table 7-3. Analytical Methods for Determining Iodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Fresh water	One liter sample is acidified with nitric acid; 5 mL sample is irradiated, filtered, and counted	INAA using Ge(Li) $\gamma$ -spectrometry	0.20 $\mu\text{g/L}$	No data	Salbu et al. 1975
Drinking water (total iodine)	$\text{K}_2\text{CO}_3$ added to sample; centrifuged to remove precipitated alkaline earth metals; iodine measured by addition of nitric acid, $\text{NaCl}$ , $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and $\text{KSCN}$	Spectrophotometry	0.2 $\mu\text{g/L}$	90–108%	Moxon 1984
Drinking water (free iodide)	$\text{K}_2\text{CO}_3$ added to sample; centrifuged to remove precipitated alkaline earth metals; iodide measured by addition of reduced amounts of nitric acid, $\text{NaCl}$ , $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ , and $\text{KSCN}$	Spectrophotometry	0.4 $\mu\text{g/L}$	89–109%	Moxon 1984
Fresh and sea waters	Samples directly injected onto a weakly anionic ion-exchange column for iodide analysis; iodate measured through reduction to iodide by ascorbic acid	HPLC with ion-selective electrode detector	2 $\mu\text{g/L}$	No data	Butler and Gershey 1984
Sea water and river water	Sample (neat or diluted) were treated with $\text{HClO}_4$ , acetone, and $\text{KMnO}_4$ ; $\text{KMnO}_4$ reduced with oxalic acid, then treated with $\text{NaS}_2\text{O}_3$ /chromic acid followed by extraction into benzene containing p-dichlorobenzene as an internal standard	GC-ECD	0.1 $\mu\text{g/L}$	No data	Maros et al. 1989
Sea water	Sample acidified with acetic acid; bromine vapor dissolved into sample; excess removed through volume reduction; titrated with iodate	Amperometric method	5 $\mu\text{g/L}$	98–112%	Barkley and Thompson 1960
Sea water (iodine)	Iodide in sample precipitated with $\text{AgNO}_3$ ; precipitate dissolved in acetic acid saturated with $\text{Br}_2$ ; filtered; filtrate reduced in volume; then reacted with starch solution and $\text{CdI}_2$	Spectrophotometry	0.025 $\mu\text{g/L}$	99% (at 10 $\mu\text{g/L}$ iodine)	Tsunogai 1971

**Table 7-3. Analytical Methods for Determining Iodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Sea water (iodate)	Iodide in sample precipitated with $\text{AgNO}_3$ ; iodate in filtrate is reduced to iodide with $\text{NaSO}_3/\text{H}_2\text{SO}_4$ , acetic acid saturated with $\text{Br}_2$ added; filtered; filtrate reduced in volume; reacted with starch solution and $\text{CdI}_2$	Spectrophotometry	0.025 $\mu\text{g/L}$	No data	Tsunogai 1971
Sea water	Sample filtered and concentrated/purified on an AG1X4 anion exchange column; $\text{I}^-$ , $\text{IO}_3^-$ , and organic iodine were isolated preferentially isolated; neutron irradiated; iodide carrier added; treated with $\text{NaNO}_2$ in $\text{HNO}_3$ ; extracted into $\text{CCl}_4$ ; back extracted into a $\text{KHSO}_3$ solution and counted	INAA using $\text{Ge(Li)}$ $\gamma$ -spectrometry	0.2 $\mu\text{g/L}$	99.5% (post-irradiation recovery)	Hou et al. 1999
Sea water and brackish water*	Sample treated with $\text{CaO}$ ; iodide oxidized with $\text{Br}_2$ in acetate buffer; excess $\text{Br}_2$ removed with sodium formate; iodate converted to iodine and titrated with $\text{NaS}_2\text{O}_3$ using starch indicator	Spectrophotometry	0.2–2,000 $\text{mg/L}$ (range of measured values)	93.6–96.7% (at 12.1–1,375 $\text{mg/L}$ )	ASTM 1995
Sea water and brackish water	Sample is acidified with $\text{HCl}$ ; iodide converted to iodine with $\text{KNO}_2$ and extracted into $\text{CCl}_4$ ; absorbance of iodine- $\text{CCl}_4$ measured at 517 nm	Spectrophotometry	0.2–2,000 $\text{mg/L}$ (range of measured values)	100–108% (at 12.1–1,375 $\text{mg/L}$ )	ASTM 1995
Sea water and brackish water	500 $\mu\text{L}$ of sample diluted to 50 ml with water plus $\text{NaNO}_2$ solution; measured potential; quantitated using standard additions	Iodide selective electrode	1–2,000 $\text{mg/L}$ (range of measured values)	102–109% (at 12.1–1,375 $\text{mg/L}$ )	ASTM 1995
Brine and thermal waters	Sample treated with 14 N $\text{H}_2\text{SO}_4$ plus 3 M $\text{H}_2\text{O}_2$ ; extracted with $\text{CCl}_4$ ; back into 0.1 mM $\text{NaS}_2\text{O}_3$ ; then iodine/methylene blue ion pair extracted into 1,2-dichloro-ethane	Spectrophotometry	10 $\mu\text{g/L}$	68% (at 0.4 mM iodine)	Koh et al. 1988

**Table 7-3. Analytical Methods for Determining Iodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Groundwater	Metals chelated with EDTA and iodate is directly measured; iodide can be indirectly measured through conversion to iodate by treatment with chlorine water	Single-sweep polarography	0.005 µg/L	No data	Whitnack 1975
Soil	Sample dried; sieved (7 mm diameter), ground; sieved (2 mm diameter); extracted with 2 N NaOH; arsenious acid added then submitted for automated analysis	As-Ce catalytic spectrophotometry	0.5 µg/g	No data	Whitehead 1979
Soil, sediments, rock	Sample dried and pulverized; mixed with V <sub>2</sub> O <sub>5</sub> and pyrohydrolyzed; evolved iodine dissolved in NaOH solution digested with acid	As-Ce catalytic spectrophotometry	0.05 µg/g (0.5 g sample size)	75–90%	Rae and Malik 1996
Coal and fly ash	<250 mg samples dried; irradiated with neutrons and then counted	INAA using Ge(Li) γ-spectrometry	0.6–1.8 µg/g (range of measured values)	No data	Germani et al. 1980
Vegetation	Sample prepared by microwave digestion using HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> ; treated with Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> or ascorbic acid solution to convert iodate to iodide	ICP-MS	100 pg/g	96–104%	Kerl et al. 1996

As-Ce catalytic spectrophotometry = arsenious-ceric ion catalytic spectrophotometry; GC-ECD = gas chromatography-electron capture detection; HPLC = high performance liquid chromatography; ICP-AES = inductively coupled plasma-atomic emission spectrometry; ICP-MS = inductively coupled plasma-mass spectrometry; IDMS = isotope dilution mass spectrometry; INAA = instrumental neutron activation analysis; UV detection = ultraviolet/visible detection

**Table 7-4. Analytical Methods for Determining Radioiodine in Environmental Samples**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air (occupational)	Air samples drawn into a regulated, constant-flow air sampler for personnel monitoring at a flow rate of 2 L/minute for several periods of 2–7 minutes; air-borne iodine was trapped in a charcoal sampling tube, then counted	Scintillation counter with NaI detector	2 fCi/mL ( $^{131}\text{I}$ )	No data	Luckett and Stotler 1980
Aerosols (occupational)	Air drawn through a 25 mm cellulose nitrate/acetate filter at a constant flow rate of 2 L/minute; filter counted	Scintillation counter with NaI detector	5 fCi/mL ( $^{125}\text{I}$ ) 0.3 fCi/mL ( $^{131}\text{I}$ )	No data	Eadie et al. 1980
Aerosols (ambient)	Aerosols were collected using an Anderson cascade impactor; filters removed from impactor and then neutron irradiated	INAA with Ge $\gamma$ -ray detector	0.24–0.26 aCi/m <sup>3</sup> (range of measured values) ( $^{129}\text{I}$ )	No data	Tsukada et al. 1991
Water	Add iodide carrier and NaOCl to 4 L sample; stir; add $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $\text{NaHSO}_3$ ; stir; filter; extract through anion exchange resin; elute iodide with NaOCl; treat with $\text{HNO}_3$ ; extract with toluene and aqueous $\text{NH}_2\text{OH}\cdot\text{HCl}$ , back extract with aqueous $\text{NaHSO}_3$ ; precipitate iodide as $\text{CuI}$	$\gamma$ -spectrometry with Ge detector	<1 pCi/L ( $^{131}\text{I}$ )	No data	ASTM 1994
Drinking water	Iodate carrier added to sample and iodate reduced to iodide with $\text{NaSO}_3$ ; iodide precipitated with $\text{AgNO}_3$ ; AgI dissolved and purified with Zn powder and sulfuric acid; iodide reprecipitated as $\text{PdI}_2$	$\beta$ - $\gamma$ coincidence scintillation system	0.1 pCi/L ( $^{131}\text{I}$ )	No data	EPA 1976, 1980

**Table 7-4. Analytical Methods for Determining Radioiodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Drinking water	Iodate carrier and tartaric acid are added to sample, HNO <sub>3</sub> added and sample distilled into NaOH solution; distillate acidified with H <sub>2</sub> SO <sub>4</sub> and oxidized with NaNO <sub>2</sub> ; extracted into CCl <sub>4</sub> ; back extracted into NaHSO <sub>3</sub> ; and iodide reprecipitated as PdI <sub>2</sub>	β-γ coincidence scintillation system	0.1 pCi/L ( <sup>131</sup> I)	No data	Krieger 1976
Fresh water	Conversion of iodine to iodide; concentrated on anion exchange resin; extracted with CCl <sub>4</sub> , water, then toluene	Liquid scintillation counter	0.3 pCi/L ( <sup>129</sup> I)	74% with 30 mg iodine carrier	Gabay et al. 1974
Fresh water	Iodide carrier added to sample; treated with HCl and sodium metabisulfite; iodide concentrated on a strong anion exchange resin with iodine carrier; <sup>125</sup> I directly detected on resin	γ-spectrometry with Ge(Li) detector and x-ray fluorescence for yield correction	30 pCi/L ( <sup>125</sup> I)	No data	Howe and Bowlit 1991
River water	Sample directly analyzed or concentrated on an anion exchange resin; eluted with nitric acid; analyzed, using indium as an internal standard	ICP-MS	0.5 pCi/L ( <sup>129</sup> I)	No data	Beals and Hayes 1995; Beals et al. 1992

**Table 7-4. Analytical Methods for Determining Radioiodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Aqueous sample	Sample concentrated on a Dowex 1x8 anion exchange resin; resin pyrolyzed; iodine adsorbed onto activated charcoal; iodine removed by heating charcoal; neutron irradiated; iodine carrier added; iodine extracted into xylene; iodide precipitated with silver	INAA with Ge(Li) detector	3.8 fCi/L ( $^{129}\text{I}$ )	50%	Anderson 1978
Water	Iodide carrier was added to samples; treated with sodium hypochlorite, purified; reduced to isolate iodine and iodine precipitated as AgI; AgI was mixed with either a niobium or ultrapure silver metal binder and dried onto stainless-steel sample holders for analysis	AMS	<0.3 pg/g ( $^{129}\text{I}$ )	No data	DOE 1994; Elmore and Phillips 1987; Elmore et al. 1980
Water and waste water	Direct count of sample	$\gamma$ -spectrometry with Ge/Li detector	<2 pCi/L ( $^{131}\text{I}$ )	92–100% at 2–94 pCi/L	ASTM 1998
Treated sewage effluent	Sample directly counted in 3.5 L aluminum beaker	$\gamma$ -spectrometry with NaI(Tl) detector	No data ( $^{131}\text{I}$ )	No data	Sodd et al. 1975
Treated sewage (influent/effluent)	Sample counted directly or first concentrated on anion exchange column after reduction of iodine to iodide in sample; eluted with acid then counted	$\gamma$ -spectrometry with NaI(Tl) detector	180 pCi/L (direct count), 0.35 pCi/L (concentrated) ( $^{131}\text{I}$ )	No data	Prichard et al. 1981

**Table 7-4. Analytical Methods for Determining Radioiodine in Environmental Samples (*continued*)**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Soil, sediments, vegetation	Sample dried; iodine extracted through combustion of soil in oxygen; iodine trapped onto charcoal after passage over hydrated manganese dioxide (HMD); neutron irradiated; Br removed through passage over HMD	INAA with Ge(Li) detector	5 aCi/g ( $^{129}\text{I}$ )	No data	Lindstrom et al. 1991; Lutz et al. 1984
Vegetables	Sample lyophilized; $\text{Na}_2\text{CO}_3$ , NaCl, and $^{131}\text{I}$ (internal standard) added; dried and ashed; treated with $\text{MnO}_2$ and evolved iodine trapped in 0.1% $\text{NaHSO}_3$ containing iodide carrier	ICP-MS	1.4 pg/g (0.24 fCi/g) ( $^{129}\text{I}$ )	88%	Cox et al. 1992
Plants	Plant samples were lyophilized and ground; $^{125}\text{I}$ added as internal standard; sample was pyrolyzed in $\text{O}_2/\text{N}_2$ stream; iodine absorbed onto charcoal; iodine liberated from charcoal by heating; isolated by distillation on cooled glass and then neutron irradiated	INAA with Ge(Li) $\gamma$ -spectrometry	18–74 fCi/g ( $^{129}\text{I}$ )	50–60%	Handl et al. 1990

AMS = accelerator mass spectrometry; ICP-MS = inductively coupled plasma-mass spectrometry; INAA = instrumental neutron activation analysis

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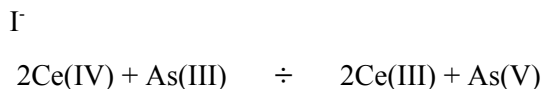
(Muramatsu et al. 1985). For example, the mass spectrometry techniques that are utilized to measure iodine in samples, such as neutron activation-noble gas mass spectrometry or accelerator mass spectrometry, provide the ability to resolve the  $^{127}\text{I}$  and  $^{129}\text{I}$  isotopes in the quantitation step and also have the required sensitivity range to measure ratios of  $10^{-10}$ – $10^{-7}$  for  $^{129}\text{I}/^{127}\text{I}$  in most environmental and biological samples (Gramlich and Murphy 1989; Schmidt et al. 1998).

The analysis of  $^{127}\text{I}$  in air is based on the quantitation of this isotope of iodine in its gaseous form ( $\text{I}_2$ ) or within aerosols or particulates, either separately or combined (Dams et al. 1970; Gäbler and Heumann 1993; Kim et al. 1981; Sheridan and Zoller 1989; Tsukada et al. 1991). The concentration of gaseous iodine in air can be determined by passing a known volume of air through a tube containing activated charcoal, followed by extraction of the iodine from the charcoal and analysis by a number of techniques, including ion chromatography (Kim et al. 1981). Both the gaseous and particulate forms of iodine can be simultaneously assessed by passing a specified volume of air through a filtering device containing a series of filters with differing pore sizes and coatings (Gäbler and Heumann 1993; Tsukada et al. 1991). Both gaseous and particulate forms of iodine are trapped on the various filter stages, depending on the type of coating and pore size of the filter stage after a calibrated amount of air is pulled through the filters. For the analysis of  $^{127}\text{I}$  on the filters, the filter is solvent extracted and the extracted iodine is analyzed by INAA (Sheridan and Zoller 1989; Tsukada et al. 1991), nondestructive neutron activation analysis (Dams et al. 1970), and isotope dilution mass spectrometry (Gäbler and Heumann 1993). Analysis of airborne  $^{125}\text{I}$ ,  $^{129}\text{I}$ , and  $^{131}\text{I}$  can also be performed using the filtering techniques described above, followed by a direct measurement by beta- or gamma-ray counting of these radioisotopes on the filter or within activated charcoal (Eadie et al. 1980; Luckett and Stotler 1980) or quantitated with more sensitive techniques ( $^{129}\text{I}$ ) such as INAA (Tsukada et al. 1991).

For the analysis of iodine in water, there is a broad array of sample preparation and detection methodologies that are available (see Tables 7-3 and 7-4). A number of methods can directly quantitate iodine or its radioactive isotopes within a water sample using spectrophotometric, ion-selective electrodes, INAA, ICP-MS, polarography, or radiochemical techniques with minimal sample preparation and good detection sensitivities ( $0.1$ – $2.0\text{ }\mu\text{g/L}$  for  $^{127}\text{I}$ ,  $< 2\text{ pCi/L}$  for  $^{131}\text{I}$ ) (ASTM 1995, 1998, Beals and Hayes 1995; Beals et al. 1992; Butler and Gershey 1984; Jones et al. 1982; Prichard et al. 1981; Salbu et al. 1975; Sodd et al. 1975; Stephenson and Motycka 1994; Whitnack 1975). Some analytical methods provide for the analysis of total iodine in the sample as well as the various iodine species in water (e.g.,  $\text{I}^-$ ,  $\text{I}_2$ ,  $\text{IO}_3^-$ , and organic iodine) (Reifenhäuser and Heumann 1990; Wong and Cheng 1998). However, poor or inconsistent recovery of some iodine species (e.g.,  $\text{I}^-$  and  $\text{IO}_3^-$ ) during the ion exchange stage of the sample preparation, which is due to both irreversible binding of these iodine species to some ion exchange resins and interference from dissolved organic carbon, often can limit the accuracy of these methods for determining iodine species in aqueous samples (Stephenson and Motycka 1994).

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One of the more commonly used assays for analyzing iodine at  $\mu\text{g/L}$  concentrations in water can be done directly using the catalytic spectrophotometric method. In the assay, iodine acts as a catalyst in the reduction of the ceric ions  $[\text{Ce(IV)}]$  by arsenous ions  $[\text{As(III)}]$ :



In the absence of iodine, the reaction is very slow ( $\sim 35$  hours), but is on the order of minutes in the presence of iodine. The changes in the reaction rate, as followed by the decay in the  $\text{Ce(IV)}$  absorbance at either 420 or 366 nm, are inversely proportional to the iodine concentration in the sample (Jones et al. 1982; Lauber 1975; Truesdale and Smith 1975). This assay has been developed into an automated process offering the advantage of large sample batch analyses (Truesdale and Smith 1975).

However, like many of the methods that are used to quantitate iodine, a number of interferences can affect the measurement of iodine by the catalytic spectrophotometric method, including background coloration, turbidity, and compounds, such as  $\text{Fe(II)}$ , that are capable of reducing  $\text{Ce(IV)}$  (Jones et al. 1982; Truesdale and Smith 1975). Thus, methods have been developed that purify iodine by first extracting iodine into an organic solvent and then back extracting the iodine into an appropriate aqueous solution for As–Ce catalytic spectrophotometric analysis (Jones et al. 1982; Whitehead 1979). Likewise, for most methods, there is often a need to preconcentrate, redox convert the various iodine species (e.g.,  $\text{I}^-$ ,  $\text{I}_2$ ,  $\text{IO}_3^-$ ), and/or isolate iodine or its radioisotopes from the sample in order to improve sensitivity or remove interfering species, as is illustrated in Tables 7-3 and 7-4. Newer techniques have been developed to improve the separate quantitation of iodine species. An example is the use of ICP-MS to quantitate iodide directly in the samples after filtering, whereas iodine is quantitated as a vapor that is evolved from the sample following treatment of the sample with potassium nitrite in sulfuric acid. This approach provides a detection limit of  $0.04 \mu\text{g/mL}$  and recoveries of 86.5–118.6% (Anderson et al. 1996)

The quantity of iodine and its radioisotopes in soil, sediments, minerals, vegetation, and biota is determined using detection methods similar to those described above (Tables 7-3 and 7-4). Analysis of iodine in samples by spectrophotometry, electrochemistry, and MS requires some form of sample digestion, either treatment in acid or pyrolysis. For most methods, sample concentration or purification is required to remove interfering species and/or improve detection sensitivity.

In the quantitation of  $^{129}\text{I}$  in soil, mineral, and biological samples by the INAA method, improvements to the INAA method for determining  $^{129}\text{I}$  have been developed to minimize the possible interferences that can occur from  $^{133}\text{Cs}(n,\alpha)^{130}\text{I}$ ,  $^{127}\text{I}(3n,\gamma)^{130}\text{I}$ ,  $^{235}\text{U}(n,f)^{129}\text{I}$  as well as neutron capture by  $^{128}\text{Te}$  and  $^{130}\text{Te}$ . The presence of bromine within a particular sample also can interfere with the quantitation of  $^{129}\text{I}$  due to the

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higher activity of  $^{82}\text{Br}$ , the small difference in the photopeak maxima for  $^{129}\text{I}$  (0.45 MeV) and  $^{82}\text{Br}$  (0.55 MeV) and chemical similarities for I and Br (Ohno 1971; Rook et al. 1975). Most of these interferences have been eliminated through the use of preirradiation separation step that involves the combustion of iodine from biological materials followed by the collection of iodine on activated charcoal (Rook et al. 1975). A postirradiation step also has been developed using an electromagnetic mass separator with a hot cathode arc ion chamber source to separate and collect sample components within a specific mass range onto an aluminum foil for subsequent quantitation by a  $\beta$ - $\gamma$  coincidence analysis system (Rook et al. 1975).

The detection limits, accuracy, and precision of any analytical methodology are important parameters in determining the appropriateness of a method to quantitate a specific analyte at the desired level of sensitivity within a particular matrix. The Lower Limit of Detection (LLD) has been adopted to refer to the intrinsic detection capability of a measurement procedure (sampling through data reduction and reporting) to aid in determining which method is best suited for the required sample quantitation (EML 1997; NRC 1984). Several factors influence the LLD, including background counting-rates, size or concentration of sample, detector sensitivity, recovery of desired analyte during sample isolation and purification, level of interfering contaminants, and, particularly, counting time. Because of these variables, the LLDs between laboratories, utilizing the same or similar measurement procedures, will vary.

The accuracy of a measurement technique in determining the quantity of a particular analyte in environmental samples is greatly dependent on the reliability of the calibrating technique. Thus, the availability of standard, certified radiation sources with known concentrations of iodine and its radioisotopes are required in order to insure the reliability of the calibration methods and accuracy of iodine measurements in environmental samples. NIST traceable standards for  $^{127}\text{I}$  can be obtained through a number of commercial sources. The primary source of certified iodine radioisotope standards is the NIST. Standard reference materials for  $^{129}\text{I}$  (SRM 4401LZ, 30 MBq [0.8 mCi]) and  $^{131}\text{I}$  (SRM 4949C, 17 kBq [0.45  $\mu\text{Ci}$ ]) are available from NIST. SRMs are also available for  $^{127}\text{I}$  measurements, including SRM 1515 (apple leaves), SRM 1547 (peach leaves), SRM 1566 (oyster tissue), SRM 1572 (citrus leaves), SRM 1573 (tomato leaves), SRM 1575 (pine needles), SRM 1577 (bovine liver), SRM 1632 (coal), SRM 1633 (fly ash), SRM 1643 (water), SRM 2704 (sediment), and SRM 2709 (soil).

### 7.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of iodine is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation

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of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of iodine.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

### 7.3.1 Identification of Data Needs

**Methods for Determining Biomarkers of Exposure and Effect.** Analytical methods with satisfactory sensitivity and precision are available to determine the levels of iodine and its radioisotopes in human tissues and body fluids.

**Exposure.** Analytical methods with satisfactory sensitivity and precision are available to determine the exposure levels of iodine and its radioisotopes in human tissues and body fluids.

**Effect.** Analytical methods with satisfactory sensitivity and precision are available to determine the levels of effect for iodine and its radioisotopes in human tissues and body fluids.

**Methods for Determining Parent Compounds and Degradation Products in Environmental Media.** Analytical methods with the required sensitivity and accuracy are available for quantitating iodine, both total and isotopic, in environmental matrices (Tables 7-3 and 7-4). Knowledge of the levels of iodine in various environmental media, along with appropriate modeling (see Chapters 2 and 4), can be used to evaluate potential human exposures through inhalation and ingestion pathways.

Whether in the environment or in the human body, iodine radioisotopes will undergo radioactive decay to form a series compounds that are also radioactive (see Chapter 3). Current analytical methods, such as mass spectrometry, have the necessary resolution and sensitivity to detect and quantitate these decay products.

### 7.3.2 Ongoing Studies

Current research studies, as provided by a search of the Federal Research in Progress (FEDRIP) database, are looking at improvements in the resolution and sensitivity of gamma ray scintillation spectrometers through the development of innovative scintillating materials. In the work proposed in the research grant entitled “Ultra-Compact Cesium Iodide - Mercuric Iodide Gamma-Ray Scintillation Spectrometer” (B.E.

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Patti, Principal Investigator), the investigators are working with CsI/HgI scintillation pairs to develop a room temperature gamma-spectrometer after having some preliminary success with the detection of the 660 keV gamma-ray from  $^{137}\text{Cs}$  (4.58% FWHM) (FEDRIP 2000). In another study entitled “Bismuth Iodide Crystal Growth” (L.A. Boatner, Principal Investigator), the investigators are working on developing techniques for growing bismuth iodide crystals for room temperature radiation detectors and testing these crystals for their efficiency and energy resolution characteristics (FEDRIP 2000).